

ON THE SOLUBILITY OF NITROGEN IN AUSTENITIC  
CHROMIUM-NICKEL AND CHROMIUM-NICKEL-MOLYBDENUM STEELS

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16. Abstract Solubility of nitrogen and effects of dissolved nitrogen and various precipitated phases were studied in steels containing 18% Cr, 14% Ni and with or without 2.5% Mo. Chromium nitride forming at grain boundaries makes the steel brittle.			
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ON THE SOLUBILITY OF NITROGEN IN AUSTENITIC  
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Hubertus Laddach, Gustav Lennartz and Günther Preis

/ 75 \*

The development of nitrogen-alloyed austenitic chromium-nickel and chromium-nickel-molybdenum steels with very low carbon contents produced significant advantages for the region of common temperatures of use. These are expressed primarily in the improvement of some mechanical properties and increased stability of structure with unaltered good corrosion resistance. Use of nitrogen as an alloying element presumes adequate knowledge of the solubility of nitrogen in the material, and we must distinguish between interstitially dissolved nitrogen and nitrogen bound as the nitride.

In a preceding work [1] we have already studied metallurgical behavior and the solubility limits of nitrogen in austenitic chromium-nickel steels with 18 to 25% Cr and 8 to 40% Ni as a function of the temperature at normal pressure. These studies will be directed toward the effect of additions of up to 2.5% molybdenum.

In contrast to the chromium-nickel steels, the chromium-nickel-molybdenum steels tend increasingly to formation of delta ferrite and to precipitation of intermetallic phases such as the chi, the sigma, and the Laves phase with increasing additions of molybdenum [2-7]. These precipitates result in changes of the properties, shown principally in an increased

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\* Numbers in the margin indicate pagination in the original foreign text.

tendency to embrittlement, in the loss of corrosion resistance, and in problems in heat-shaping [3, 8, 9, 10].

From addition of nitrogen to chromium-nickel-molybdenum steels we can expect not only the well-known expansion of the  $\gamma$  phase space [11] but also an effect on the rate of formation and the resistance range of the intermetallic phases. Even from the older literature [12, 13] we can find that the alloying element nitrogen delays the rate of formation of the sigma phase and shifts the resistance range to lower temperatures or to higher chromium contents. H. Thier, A. Bäuml and E. Schmidtmann [14] made a detailed study of the effect of nitrogen on the precipitation behavior of a steel with 17% Cr, 13% Ni and 4.5% Mo. They observed that nucleation of the above-mentioned phases is generally hindered by nitrogen.

In the present work, we investigate the metallurgical and material behavior of nitrogen- and molybdenum-alloyed austenitic chromium-nickel steels at temperatures above 600°C and compare them with the corresponding molybdenum-free materials. / 76

The following deliberations contain the experimental results on the solubility of nitrogen in these alloys as well as the chemical composition and crystallographic structure of the phases separating. The effect of the precipitates on the technological properties will be shown by means of notch impact strength tests.

### 1. Conduct of the Experiment

The studies were done on rust- and acid-resistant steels of the usual commercial chemical composition based on 18% Cr and 14% Ni (Table 1). In order to limit as much as possible the effect of the carbon content, we attempted to get a value

of less than 0.02% C. The melts were fused in a basic induction furnace and the nitrogen introduced by means of nitrogen-containing ferrochrome with 3.37% N.

Table 1. CHEMICAL COMPOSITION OF THE MATERIALS STUDIED.

Steel No.	Mass Content in %						
	C	Si	Mn	Cr	Ni	Mo	N
1	0,017	0,52	1,46	17,52	14,63	n. b.	0,02
2	0,017	0,41	1,51	18,22	14,13	n. b.	0,25
3	0,015	0,53	2,06	17,88	14,11	2,42	n. b.
4	0,016	0,35	1,56	17,23	13,08	2,28	0,09
5	0,015	0,38	1,57	17,11	13,04	2,29	0,12
6	0,020	0,43	1,60	17,23	13,09	2,31	0,21
7	0,020	0,42	1,58	18,00	14,26	2,46	0,21

Table 2. SCHEME OF THE HEATING EXPERIMENTS DONE.  
(Solution heat treatment: 30 min 1150°C/water)

Heating Temperature °C	Heating Duration									
	hrs									
1000	0,1	0,2	0,5	1	5	20	100	500	2000	
950	0,1	0,2	0,5	1	5	20	100	500	2000	
900	0,1	0,2	0,5	1	5	20	100	500	2000	
850	0,1	0,2	0,5	1	5	20	100	500	2000	10 000
800				1	5	20	100	500	2000	10 000
750 *)				1	5	20	100	500	2000	10 000
700 **)				1	5	20	100	500	2000	10 000
650 **)				1	5	20	100	500	2000	10 000

\* Precipitation done in both the solution heat treated state and after additional cold forming.

\*\* Precipitation only after additional cold forming

Starting from a precipitate-free structure condition following a solution heat treatment in a salt bath at 1150°C followed by water quenching, the experimental material was heated isothermally according to the scheme shown in Table 2. The brief heatings up to 5 hours were done in the salt bath, and the longer heat treatments in an electrically heated muffle furnace with air excluded. As the precipitation process is extremely slow at low temperatures, the samples precipitated at 650, 700 and 750 °C were first cold formed by 35% after a solution heat treatment.

The experimental results needed for completion of this work for Steel number 3 were taken from a previous work by G. Lennartz [3]. The usual industrial solution heat treatment of 1050°C/water departs only insignificantly from the usual heating in these experiments. The isothermal precipitation treatments are identical except for the short-term experiments.

The precipitated samples were studied metallographically. After an even etching with mixed acids, the chi and sigma phases were characterized with the Murakami solution.

For analytical determination of their chemical composition and roentgenographic identification of their crystallographic structure, the precipitates were separated from the ground mass by electrochemical isolation in an electrolyte consisting of 25 parts by volume concentrated hydrochloric acid, 25 parts methyl alcohol and 50 parts isopropyl alcohol. Because, according to H. Wiegand and M. Doruck [15], the sigma phase is dissolved in the electrolyte used here, when it appeared the isolation was done in a solution consisting of 1 part by volume of concentrated nitric acid, 5 parts acetic acid and 94 parts methyl alcohol. Depending on the amount of isolate expected, the isolation lasted 24 or 48 hours, with the anodic current density adjusted

to 10 mA/cm<sup>2</sup>. The isolation of the sigma phase was done potentiostatically at -100 mV E<sub>c</sub> (about 5 mA/cm<sup>2</sup>).

After conclusion of the isolation, the content of iron, chromium, nickel, molybdenum and nitrogen was determined photometrically using well known methods. The nitrogen soluble in the ground mass was determined in order to complete the investigations in the electrolytes.

The crystallographic structures of the phases were identified by X-ray diffraction by the Debye-Scherrer method using chromium-K<sub>α</sub> radiation and a vanadium filter. The assignment was done on the basis of the statements in the ASTM chart.

The mechanical properties were tested by means of the notch impact resistance, which is affected even by the finest precipitates, as a function of the heating duration.

## 2. Results of the Investigation

In the subsequent presentation of the results of the investigation, we pay particular attention to comparison of the metallographic behavior of nitrogen-alloyed austenitic chromium-nickel and chromium-nickel-molybdenum steels. In order to be able to characterize the effect of nitrogen up to 0.2% N, steels of the same chemical composition, not alloyed with nitrogen, were included in the investigations.

/ 77

### 2.1 Solubility of Nitrogen in the Steels Investigated

After approaching the state of thermodynamic equilibrium by long-term heating, the solubility of nitrogen in the austenitic chromium-nickel and chromium-nickel-molybdenum steels was determined in the temperature range of 650 to 1000 °C.

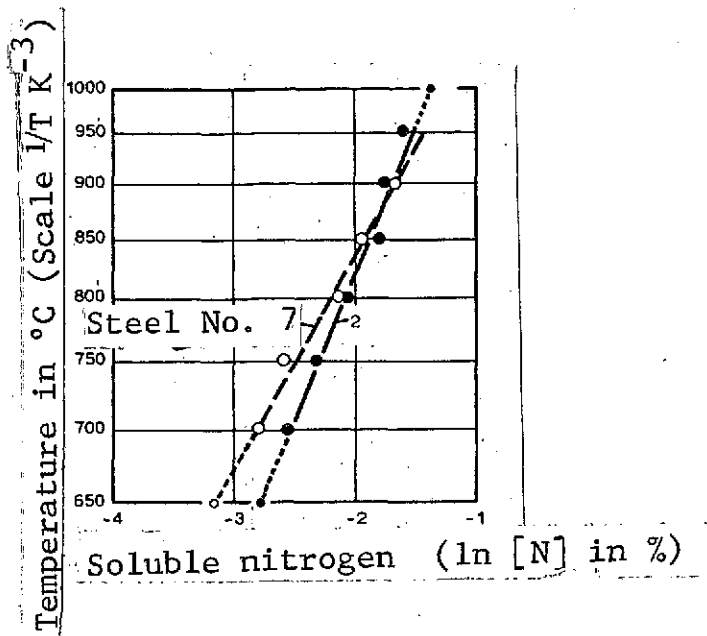


Figure 1. Maximum solubility of nitrogen in Steels No. 2 and 7 as functions of the temperature.

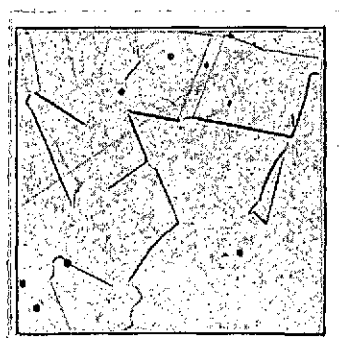
Figure 1 shows the soluble nitrogen contents of Steels No. 2 and 7 as functions of the temperature. It is striking that the molybdenum-free steel No. 2 shows a higher nitrogen solubility below 900°C than does the molybdenum-alloyed steel No. 7, while it can be considered as certain that the solubility relations reverse above 900°C and the chromium-nickel-molybdenum steel can intersperse increasingly higher nitrogen contents in the lattice with rising temperature. The extreme values in the temperature range studied were partially extrapolated numerically on the basis of the linear relationship, because at 650°C the duration of precipitation was not adequate to attain thermodynamic equilibrium, and because the nitrogen content added to the melts at the highest temperatures was below the solubility limit. Extrapolation of the solubility limit of nitrogen in molybdenum-alloyed steels is only conditionally possible because of the total precipitation behavior.



Beginning with an approximately equal matrix composition in the solution-annealed state, except for the addition of molybdenum, a soluble nitrogen content of 0.06% N is measured for steel No. 2 at 650 °C, and a content of 0.04% N for steel No. 7. with 2.5% Mo. An increase of the maximum solubility can be established with rising temperature for both materials. The solubility in the molybdenum-containing steel No. 7 rises faster. Between 850 and 900°C it exceeds the solubility of steel No. 2. At 900°C the soluble nitrogen content of the molybdenum-containing steel No. 7 is distinctly above that for the steel No. 2, not alloyed with molybdenum, for which we can give an extrapolated value of 0.25% N at 1,000°C. For steel No. 7 no extrapolation above 900°C was done, because here it is necessary to consider the transition from the multiphase to the single-phase region.

## 2.2 Precipitation Processes During the Isothermal Heating in The Temperature Range From 650 to 1000°C

After solution heat treatment at 1150°C, all the steels show a homogeneous austenitic structure (Figure 2).



Etchant: mixed acid

500:1

Figure 2. Structure of Steel No. 7 in the solution-annealed state.

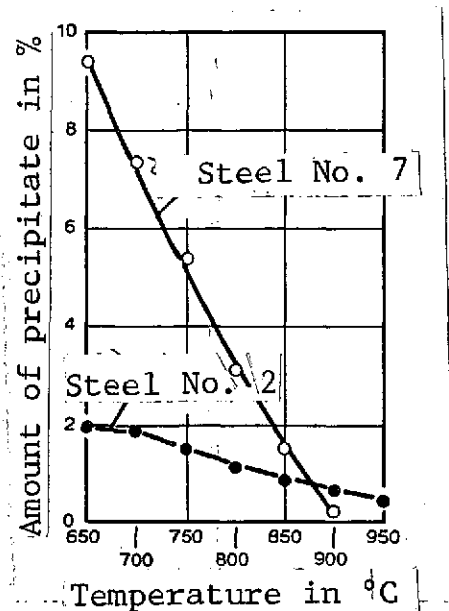


Figure 3. Total amount of precipitate in Steels No. 2 and 7 as a function of the temperature, after heating to equilibrium.

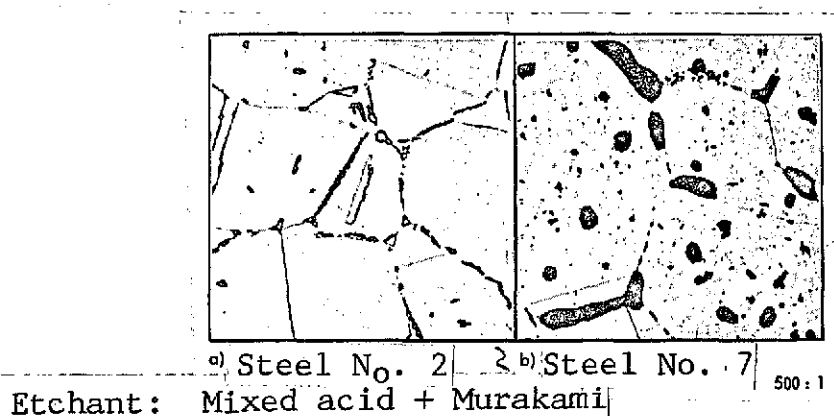


Figure 4. Structure development of Steels No. 2 and 7 after a heat treatment of 1150°C 30 min/water and 800°C 10,000 hrs/water.

On isothermal precipitation in the temperature range from 650 to 1000°C phases separate. Their composition, amount, position and form have been determined through the temperature, heating duration, and alloy composition. It is clear that the precipitation behavior of the nitrogen-containing steels is considerably affected by addition of 2.5% molybdenum, similar to the materials of this type not alloyed with nitrogen. The total amount of precipitate in Steels No. 2 and 7, shown comparatively in Figure 3 as a function of the temperature, characterizes the effect of the molybdenum addition. The proportion of the phase forming in Steel No. 7, up to equilibrium, is increasingly greater with falling temperature than in Steel No. 2. With a metallographic consideration of the structure (Figure 4), we can establish that along with the amount of precipitate there are also differences in the number of the phases and in their positions. While only one phase can be observed in Steel No. 2, formed preferentially at the grain boundaries and incoherent twinning boundaries, several phases can be detected in the structure of Steel No. 7. These separate within the grain as well as at the grain boundaries.

### 2.2.1 Effect of heating duration

The change with time of the state of the structure in Steels No. 2 and 7 is shown metallographically in Figure 5 for the precipitation temperature of 800°C. The homogeneous structure of this material shown in Figure 2 changes as follows with increasing duration of precipitation: After a heating duration of 1 hour, fine, not connected particles can be detected at the grain boundaries (Figures 5a and 5e). The first deposits at the grain boundaries could be shown even after 30 minutes. It appears that the precipitation begins first in the nitrogen-alloyed chromium-nickel steel. Also, the amount of precipitate in this material after a heating duration

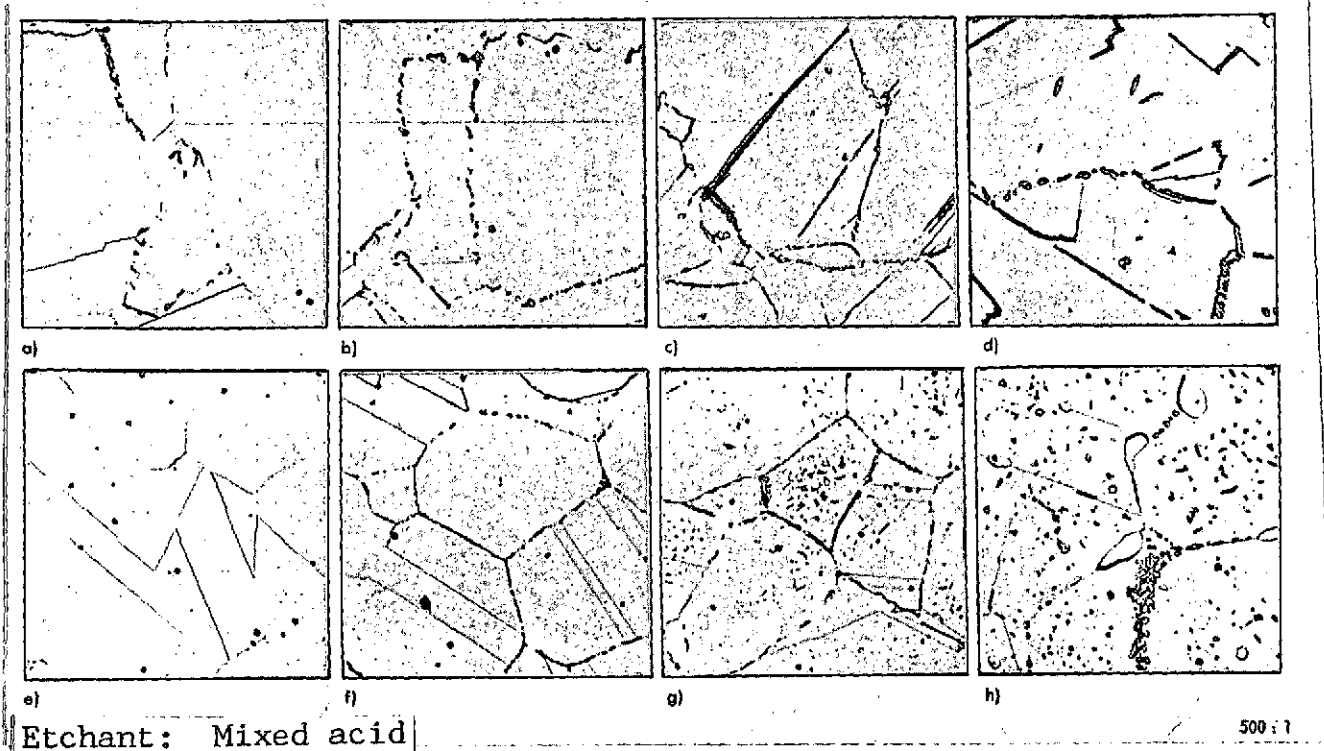


Figure 5. Effect of heating duration on structure development in Steel No. 2 (Figure a to d) and Steel No. 7 (Figure e to h) at a temperature of 800°C.  
 a and e: 1150°C 30 min/water + 800°C 1 hr/water  
 b and f: 1150°C 30 min/water + 800°C 20 hrs/water  
 c and g: 1150°C 30 min/water + 800°C 500 hrs/water  
 d and h: 1150°C 30 min/water + 800°C 10,000 hrs/water.

of 20 hours (Figure 5b) is distinctly above that of the molybdenum-alloyed comparison steel (Figure 5f).

The precipitates in Steel No. 2 appear principally at the energetically preferred sites such as grain boundaries and twinning boundaries. In Steel No. 7, by contrast, we can after 20 hours of heating (Figure 5f) already detect the first particles irregularly distributed in the grain. Their proportion grows considerably with increasing duration of precipitation (Figures 5g and 5h).

The amount of the precipitates increases with the duration of heating. The observations made initially change basically and the nitrogen-alloyed chromium-nickel-molybdenum steel shows more precipitates, at least beyond a heating duration of 100 hours. After 10,000 hours of isothermal heating, the initially fine and variously formed particles coagulate (Figures 5d and 5h). Here it must be noted that forming-in occurs already after 500 hours in steel No. 2 (Figure 5c). The formed-in particles reach a significant size primarily in the molybdenum-alloyed Steel No. 7 (Figure 5h).

The chemical compositions of the precipitates and their change with time differ greatly (Figures 6 and 7). In steel No. 2 we can observe principally the precipitation of chromium and nitrogen in a ratio which remains constant while the amount increases with the duration of heating (Figure 6a).

/ 79

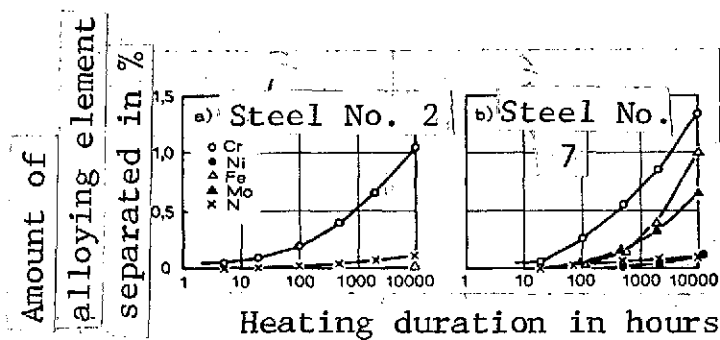


Figure 6. Effect of the heating duration on the course of precipitation in the nitrogen-alloyed Steels No. 2 and 7 at 800°C.

The composition of the isolate from Steel No. 7 is considerably more complex, by comparison (Figure 6b). While at first, likewise, only chromium and nitrogen can be observed in the same ratio as above, after 100 hours molybdenum as well as somewhat less iron can be detected in the residue. The

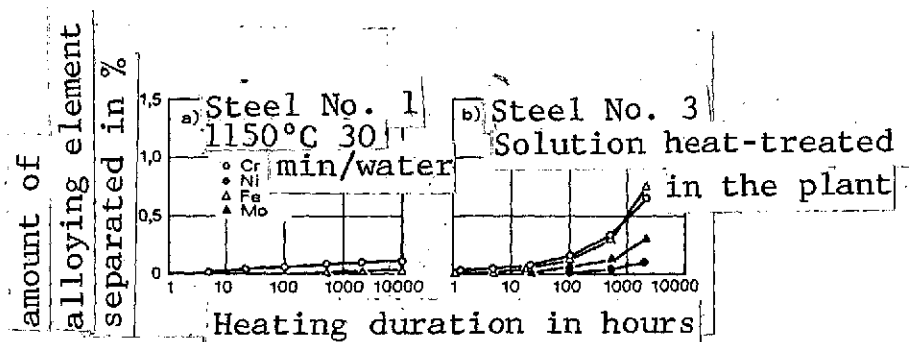


Figure 7. Effect of the duration of heating on the course of precipitation in Steels No. 1 and 3, which are not alloyed with nitrogen, at 750°C.

precipitated chromium content rises and no longer matches the previous chromium-nitrogen ratio. After 500 hours of heating we can also observe an increased separation of the elements molybdenum and iron, with the iron content now increasingly predominating. Nickel can also be determined in the isolate.

In order to characterize the effect of the nitrogen addition, Figure 7 shows the composition of the isolate from the Steels No. 1 and 3, not alloyed with nitrogen, as functions of the heating duration. While only minor amounts of chromium and, after longer precipitation, also of iron, precipitate in chromium-nickel Steel No. 1 (Figure 7a), in the molybdenum-alloyed Steel No. 3 the amount of precipitate is considerably greater again than in the nitrogen-alloyed materials. Along with chromium and iron they also contain molybdenum and nickel (Figure 7b). In contrast to the nitrogen-alloyed Steel No. 7, with roughly comparable proportions of nickel and molybdenum in Steel No. 3, less chromium separates, but considerably more iron.

## 2.2.2 Effect of the temperature

Figure 3 shows the course of the amounts of precipitates from the nitrogen-containing Steels No. 2 and 7 after heating to approximate thermodynamic equilibrium, as a function of the temperature. The precipitates have compositions as shown in Figure 8.

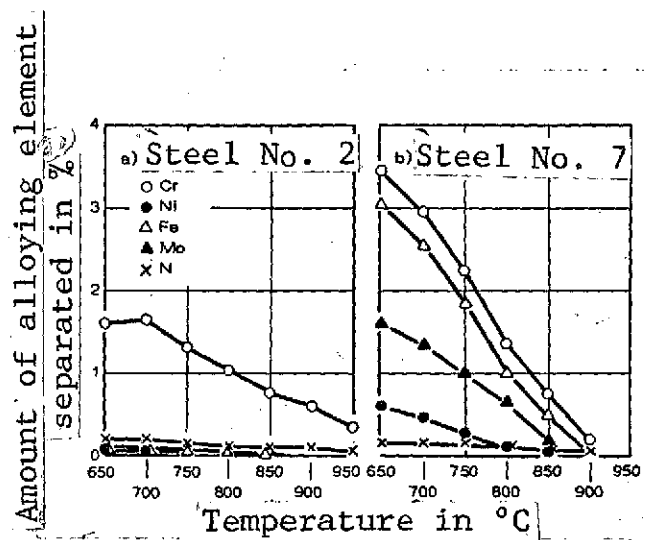


Figure 8. Effect of the temperature on the precipitation behavior of the nitrogen-alloyed Steels No. 2 and 7 after heating to thermodynamic equilibrium.

In Steel No. 2 (Figure 8a) the precipitates exhibit increasing contents of chromium and nickel with falling temperature, while the ratio of these elements remains approximately constant in the entire temperature range. The proportions of iron and nickel are negligible.

For the molybdenum-alloyed Steel No. 7 we can establish that only minor contents of chromium separate at 900°C. These are in a definite ratio to the nitrogen content (Figure 8b).

The chromium content in the isolate increases significantly only when iron and molybdenum separate. With falling temperature the proportions of the elements mentioned increase, corresponding to the amount of precipitate, with the chromium content always the highest. The proportion of the iron in the residue runs approximately parallel with this, with the ratio of these two elements changing to favor the iron at lower temperature. The content of molybdenum separating below 900°C is significant. At 650°C, more than half of the added magnesium is withdrawn from the ground mass. With decreasing temperature, nickel is also taken up increasingly by the intermetallic phases forming at these temperatures. The amount of nitrogen separated increases with decreasing temperature, corresponding to the degree of supersaturation.

The composition of the isolates from the nearly nitrogen-free Steels No. 1 and 3 can be seen from Figure 9. In the

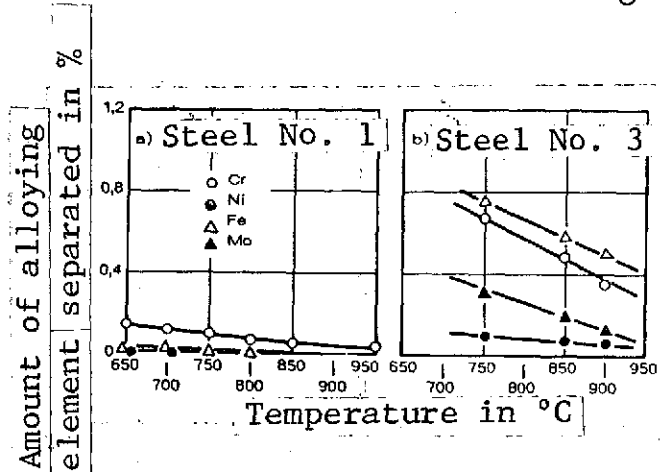


Figure 9. Effect of the temperature on the precipitation behavior of the non-nitrogen-alloyed Steels No. 1 and 3 (heating duration: Steel No. 1 to equilibrium, Steel No. 3: 2,000 hrs).



stable austenitic chromium-nickel Steel No. 1 only minor amounts of chromium separated, and also traces of iron and nickel below 800°C (Figure 9a). For the molybdenum-containing Steel No. 3, only the tendency can be shown, because the heating duration of 2,000 hours was not adequate for equilibration.

Below 950°C we can observe greater separation in the sequence of nickel, molybdenum, chromium and iron (Figure 9b). It should be particularly noted that in contrast to the nitrogen-alloyed Steel No. 7, here the proportion of iron separated in the entire temperature range is above the amount of chromium which separates.

### 2.2.3 Identification of the separated phases

The separated phases were concentrated by using electrochemical isolation methods. The chemical compositions of these isolated components of the structure, and their crystallographic structure, gave the phase distribution shown in Table 3, corresponding approximately to thermodynamic equilibrium. Estimation of the phase proportions is not possible for the molybdenum-containing steels because intermetallic phases which are partially very similar in their chemical composition form.

The chrom-nickel Steel No. 1, which is not alloyed with nitrogen, contains small amounts of a precipitate of the face-centered cubic carbide  $M_{23}C_6$  which could be detected up to 850°C in spite of the slight carbon content in the steel. Analytical determination of the carbon content was not possible because of the small amount of the isolate.

In the nitrogen-alloyed chromium-nickel Steel No. 2 only the hexagonal chromium nitride,  $Cr_2N$ , could be identified in the temperature range studied up to 950°C. Its formation was

/ 81

Table 3. DISTRIBUTION OF THE ELEMENTS IN THE PRECIPITATES AFTER ISOTHERMAL PRECIPITATION TO THERMODYNAMIC EQUILIBRIUM

Steel No.	Heating Temperature	Mass content of the Precipitates in %					Phase distribution				
		Fe	Cr	Ni	Mo	N					
1	650	6,5	87,0	1,0	—	—	$M_{23}C_6$				
	700	6,0	88,0	0,5	—	—	$M_{23}C_6$				
	750	5,0	89,0	—	—	—	$M_{23}C_6$				
	800	4,5	89,5	—	—	—	$M_{23}C_6$				
	850	4,5	89,5	—	—	—	$M_{23}C_6$				
2	650	—	89,1	—	—	10,1	$(M_{23}C_6)$	$Cr_2N$			
	700	—	90,1	—	—	9,8	$(M_{23}C_6)$	$Cr_2N$			
	750	—	89,9	—	—	10,1	$(M_{23}C_6)$	$Cr_2N$			
	800	—	89,8	—	—	10,2	$(M_{23}C_6)$	$Cr_2N$			
	850	—	89,2	—	—	10,8	$(M_{23}C_6)$	$Cr_2N$			
	900	—	89,4	—	—	10,6	$(M_{23}C_6)$	$Cr_2N$			
	950	—	90,2	—	—	9,7	$(M_{23}C_6)$	$Cr_2N$			
3	650	23,3	53,0	4,3	19,4	—	$M_{23}C_6$	Laves-Phase	$\sigma$ -Phase	( $\chi$ -Phase)	
	700	36,5	40,8	4,9	17,8	—	$M_{23}C_6$	Laves-Phase	$\sigma$ -Phase	( $\chi$ -Phase)	
	750	47,9	31,5	5,5	15,1	—	$(M_{23}C_6)$	Laves-Phase	$\sigma$ -Phase	$\chi$ -Phase	
	800	50,0	30,2	5,9	13,9	—	$(M_{23}C_6)$	Laves-Phase	$\sigma$ -Phase	$\chi$ -Phase	
	850	51,2	30,0	6,0	12,8	—	$(M_{23}C_6)$		$\sigma$ -Phase	$\chi$ -Phase	
	900	51,2	30,2	7,1	11,5	—	$(M_{23}C_6)$		$\sigma$ -Phase	$\chi$ -Phase	
4	650	43,9	33,6	6,1	16,0	0,4	$(M_{23}C_6)$	$(Cr_2N)$	Laves-Phase	$\sigma$ -Phase	( $\chi$ -Phase)
	700	45,2	31,4	6,3	16,8	0,3	$(M_{23}C_6)$	$(Cr_2N)$	Laves-Phase	$\sigma$ -Phase	( $\chi$ -Phase)
	750	48,2	29,4	4,7	17,7	—	$(M_{23}C_6)$		Laves-Phase	$\sigma$ -Phase	$\chi$ -Phase
	800	48,3	27,9	3,9	19,9	—	$(M_{23}C_6)$				$\chi$ -Phase
	850	48,5	29,4	2,5	19,6	—	$(M_{23}C_6)$				$\chi$ -Phase
5	650	41,9	33,3	6,0	18,0	0,8	$(M_{23}C_6)$	$Cr_2N$	Laves-Phase	$\sigma$ -Phase	( $\chi$ -Phase)
	700	42,4	34,1	4,5	18,4	0,6	$(M_{23}C_6)$	$Cr_2N$	Laves-Phase	$\sigma$ -Phase	( $\chi$ -Phase)
	750	41,7	35,3	4,1	18,4	0,5	$(M_{23}C_6)$	$(Cr_2N)$	Laves-Phase	$\sigma$ -Phase	$\chi$ -Phase
	800	48,7	28,7	2,8	19,8	—	$(M_{23}C_6)$				$\chi$ -Phase
	850	48,2	29,4	1,9	20,4	—	$(M_{23}C_6)$				$\chi$ -Phase
6	650	32,7	38,8	6,4	20,2	1,9	$(M_{23}C_6)$	$Cr_2N$	Laves-Phase	$\sigma$ -Phase	( $\chi$ -Phase)
	700	32,8	39,9	4,1	21,0	2,2	$(M_{23}C_6)$	$Cr_2N$	Laves-Phase	$\sigma$ -Phase	( $\chi$ -Phase)
	750	33,2	41,2	3,8	19,1	2,7	$(M_{23}C_6)$	$Cr_2N$	Laves-Phase	( $\sigma$ -Phase)	$\chi$ -Phase
	800	34,8	40,4	2,9	18,1	3,8	$(M_{23}C_6)$	$Cr_2N$			$\chi$ -Phase
	850	13,3	69,1	1,3	8,0	8,3	$(M_{23}C_6)$	$Cr_2N$			$\chi$ -Phase
	900	3,8	82,9	—	3,5	9,8	$(M_{23}C_6)$	$Cr_2N$			
7	650	34,4	38,8	6,9	18,3	1,6	$(M_{23}C_6)$	$Cr_2N$	Laves-Phase	$\sigma$ -Phase	( $\chi$ -Phase)
	700	34,7	39,2	6,2	17,9	2,0	$(M_{23}C_6)$	$Cr_2N$	Laves-Phase	$\sigma$ -Phase	( $\chi$ -Phase)
	750	34,3	40,6	4,7	17,9	2,5	$(M_{23}C_6)$	$Cr_2N$	Laves-Phase	( $\sigma$ -Phase)	$\chi$ -Phase
	800	33,2	39,9	3,5	20,5	2,9	$(M_{23}C_6)$	$Cr_2N$			$\chi$ -Phase
	850	31,3	47,9	2,8	13,5	4,4	$(M_{23}C_6)$	$Cr_2N$			$\chi$ -Phase
	900	4,1	81,9	—	4,1	9,9	$(M_{23}C_6)$	$Cr_2N$			

deducible on the basis of the ratio of chromium and nitrogen in the isolate. Because of the slight solubility of carbon in this steel we must also assume that the chromium-rich carbide,  $M_{23}C_6$ , has also precipitated, but it was impossible to demonstrate it roentgenographically because of the very small amount.

In the molybdenum-containing Steel No. 3 we have demonstrated the Laves, sigma and chi phases along with the carbide  $M_{23}C_6$ , which here must be considered a mixed carbide of the form  $(CrFe)_{21}Mo_2C_6$ . The proportion of the chi phase is probably very small. The range of existence for the Laves phase extends to about temperatures between 800 and 850°C, while the sigma phase and, in particular, the chi phase are resistant to above 900°C.

The phase spaces of these intermetallic phases are considerably affected by an ordinary nitrogen content of some 0.2% N, as the studies on Steel No. 7 show. The existence ranges of the sigma, chi and Laves phases are generally shifted toward lower temperatures, with the range of precipitation of the chromium-rich sigma phase the most severely narrowed. The nitrogen supersaturation of the ground mass, present to above 900°C, also leads to separation of the chromium nitride,  $Cr_2N$ , along with the expected carbide,  $M_{23}C_6$ .

#### 2.2.4 Effect of heating duration and temperature

Figure 8 shows the course of precipitation in Steels No. 2 and 7 for thermodynamic equilibrium, as a function of the temperature. After a heating duration of 500 hours we get the precipitation curve for these materials which is shown in Figure 10.

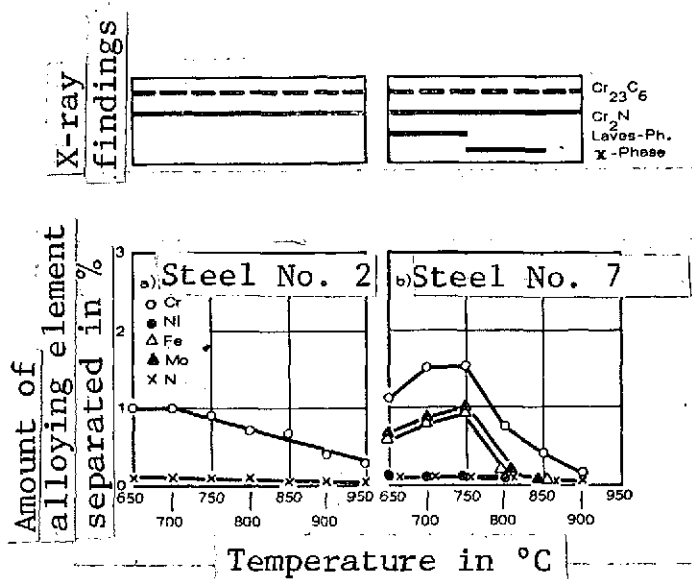


Figure 10. Effect of the temperature on the precipitation processes in the nitrogen-alloyed Steels No. 2 and 7 after heating for 500 hours.

For Steel No. 2, we can find no noteworthy changes in the precipitation behavior as a function of temperature and heating duration, except for the lower amount of nitride (Figure 10a).

Comparison of Figures 8b and 10b gives at least a partial conclusion about the precipitation kinetics of the phases appearing in the nitrogen-alloyed chromium-nickel-molybdenum Steel No. 7. First, it is striking that below 750°C the phase formation is in general considerably delayed. At equilibrium, along with the high chromium content, we can also find a high proportion of iron in the isolate, which is far above the molybdenum content. In contrast to that, we can demonstrate a lower iron content, in comparison with molybdenum, after 500 hours of heating. This differing chemical composition of the total amount of precipitates after different heating times indicates different intermetallic phases or a changed phase distribution. At 900°C only the chromium nitride,  $\text{Cr}_2\text{N}$ , can be demonstrated both after 500 hours and after

10,000 hours. The formation of this nitride could occur after relatively short heating over the whole temperature range, and could precede the beginning of separation for all other phases. The chi phase, for which we can state an upper limit of about 850°C, can already be observed at this temperature, at least after 500 hours. Below 750°C this time is no longer sufficient for the formation of the chi phase. In this lower temperature range, the Laves phase appears in its place after 500 hours.

The sigma phase, having an existence range of up to 750°C in these steels, thus forms only after a heating duration of more than 500 hours, because after this duration of precipitation it was still not roentgenographically detectable.

### 2.3 Effect of Increasing Nitrogen Contents in Chromium-Nickel-Molybdenum Steels on the Precipitation Behavior

The total amount of precipitate in the molybdenum-containing steels remains nearly independent of the nitrogen addition at 750°C and a heating duration of 2,000 hours, up to contents of 0.20% N (Figure 11). We can, however, establish a change in the chemical composition of the isolate with increasing nitrogen contents. As the nitrogen contents in the ground mass rise, the chromium content in the isolates passes through a minimum and then rises considerably, while the iron content shows an approximately opposite course. The molybdenum content rises slightly and continuously. The nickel content decreases correspondingly. Nitrogen can be demonstrated only after its solubility in the matrix is exceeded and then increases, corresponding to the degree of supersaturation. On the basis of the intensities of the diffraction reflections in the X-ray fine structure study, it can be stated that neither the Laves phase nor the chi phase, both of which appear at 750°C, are affected by higher nitrogen contents, while the sigma phase could be shown only very weakly above nitrogen contents of about 0.12%.

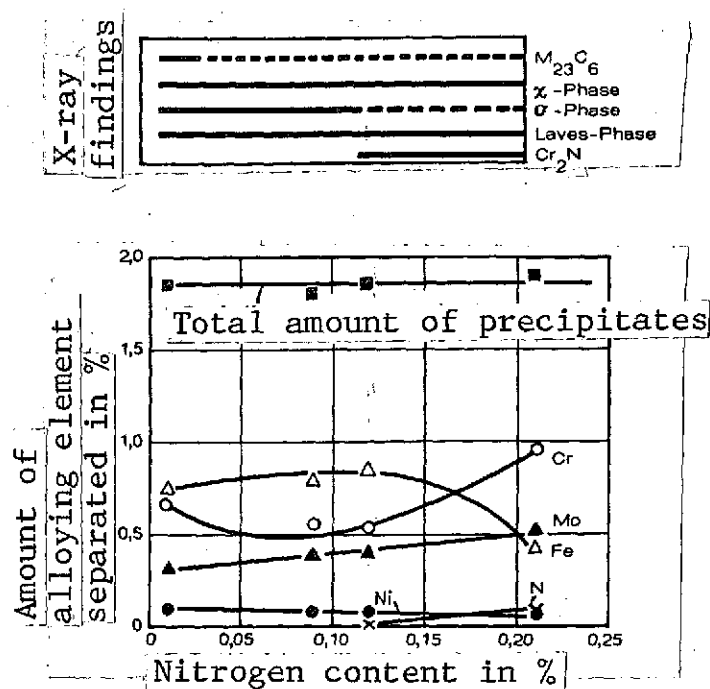


Figure 11. Effect of rising nitrogen content on the precipitation process in chromium-nickel-molybdenum steels after a heating duration of 2,000 hours at 750°C.

A comparison of the existence ranges of the possible inter-metallic phases in Steels No. 3 to 6 (Table 3) indicates that nitrogen additions of 0.09% (Steel No. 4) already suffice to shift the upper temperature limit of the phase spaces to lower temperatures. It appears that higher nitrogen contents in the ground mass (Steels No. 5 and 6) no longer affect the range of resistance notably.

### 3.4 Effect of the Precipitates on the Notch Impact Strength

The strength properties, especially the notch impact strength, are strongly affected by precipitation processes. The nature, form and position of the precipitates are of decisive significance for the extent of the embrittlement.

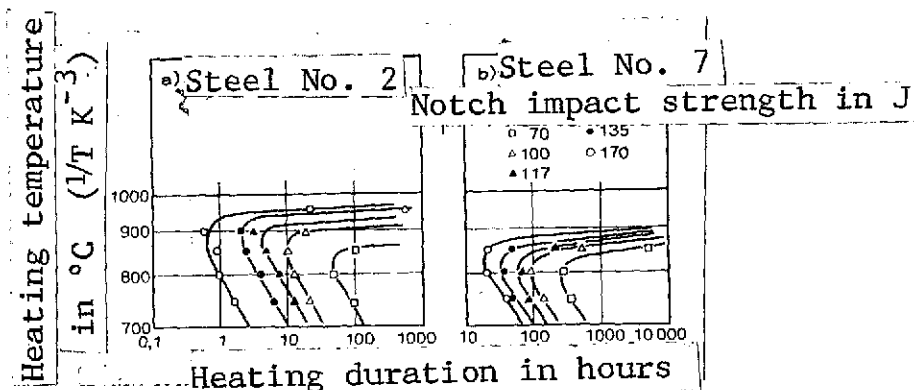


Figure 12. Effect of heating duration and heating temperature on the notch impact strength of the nitrogen-supersaturated Steels No. 2 and 7.

Curves for the same notch impact strength are plotted for Steels No. 2 and 7 in the temperature-time diagram of Figure 12. From these curves, we can see the effect of the temperature, the heating duration, and the nitrogen present in the supersaturated solution, along with the effect of the molybdenum addition of about 2.5% Mo on the notch impact strength at room temperature. Because of the precipitation of chromium nitride (Figure 12a) the notch impact strength decreases with the duration of precipitation and, thus, with the amount of precipitation. The drop in strength is slower at lower temperatures.

Through the addition of 2.5% Mo, the embrittlement behavior changes, with approximately the same notch impact strength of over 210 J in the solution-annealed state, in such a way that the comparable iso-notch-impact-strengths are shifted to lower temperatures and also to longer heating times (Figure 12b).

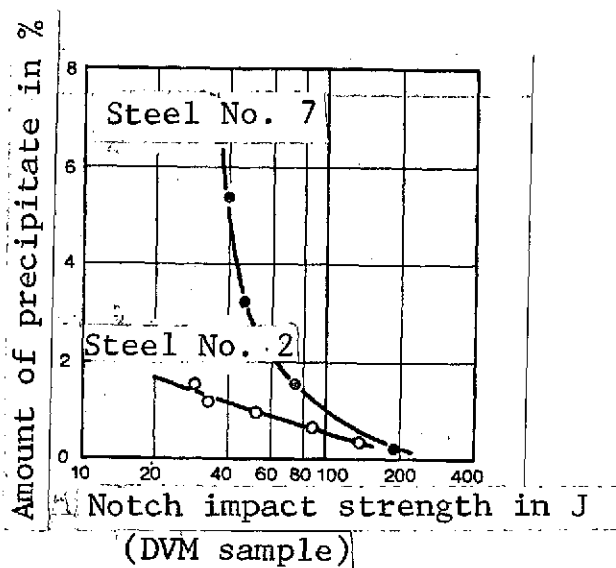


Figure 13. Relation between the total amount of precipitate and the notch impact strength for Steels No. 2 and 7.

If the amount of the precipitate after heating to equilibrium in the temperature range from 750 to 950°C is plotted versus the notch impact strength, (Figure 13), the differences in the embrittlement behavior for the two materials become clear. The amounts of precipitate which produce the same decreases in the notch impact strength are far greater in the nitrogen-alloyed chromium-nickel-molybdenum Steel No. 7 than in the nitrogen-alloyed chromium-nickel Steel No. 2.



#### 4. Discussion of the Experimental Results

Nitrogen, like carbon or boron, is embedded interstitially in the elemental lattice of metals and alloys. The solubility limit for nitrogen in metallic materials depends on the temperature and the chemical composition of the ground mass.

The chromium-nickel and chromium-nickel-molybdenum steels / 83 which were studied show an increasing solubility for nitrogen with rising temperature in the temperature range of 650 to 1,000°C and beyond at least to the solution annealing temperature of 1,150°C in the state of thermodynamic equilibrium. For the stable austenitic chromium-nickel steels, a linear relation applies as a first approximation. It can also be plotted qualitatively over the homogeneous range of the molybdenum-containing materials of this type.

In the chromium-nickel-molybdenum steels studied, the nitrogen solubility in the homogeneous austenitic phase region above 850°C is higher than in the molybdenum-free steels with the same chromium and nickel contents. Experimental demonstration of these observations was impossible above 900°C because the nitrogen content of 0.21 %N is below the solubility limit for these materials. But an increase of nitrogen solubility with molybdenum content has already been shown in a work by H. Schenck, M. G. Froberg and F. Reinders [16] for the austenite region of the two-material system iron-molybdenum. This regularity which has been established for the binary system could also be valid in iron-rich homogeneous systems of materials with the same crystallographic structure. In addition, the transferability for the elements chromium and nickel has already been shown [1]. The fundamental electron-theoretical significance of the solubility relations, such as has been presented by D. Cosma [17], under the assumption that the occupation of the outer d-electron shell determines the solubility, gives comparable

conditions for chromium, the solubility-increasing effect of which is well known, and for molybdenum. As elements having outer d-electron shells less completely occupied in comparison to iron increase the solubility of nitrogen in these materials, we can deduce that chromium and molybdenum will have the same qualitative solubility-increasing mode of action, as their 3d and 4d electron shells are occupied by the same numbers of electrons. On the basis of these considerations, there is necessarily a higher nitrogen solubility for the molybdenum-alloyed materials in the homogeneous phase space at the same chromium and nickel contents.

Below 900°C, intermetallic phases separate in the nitrogen-alloyed chromium-nickel-molybdenum steels. This changes the matrix composition as a function of the temperature. But the contents of chromium, molybdenum and nickel in the ground mass are decisive for the solubility of nitrogen in these steels. It can be seen from Figure 8b that along with minor amounts of nickel and higher proportions of iron, it is exactly the elements chromium and molybdenum which separate. This is related both to a depletion of the matrix in chromium and molybdenum and an increase in the nickel content. The chromium and nickel depletion, as well as the nickel enrichment in the matrix, are in the same direction and lead to a reduction of the solubility. In general, it can be determined that the solubility limit of the nitrogen in the multi-phase space follows that for the chemical composition of the ground mass at equilibrium.

Nitrogen additions which exceed the solubility for this material form nitrides. Only the hexagonal chromium nitride,  $\text{Cr}_2\text{N}$ , could be identified above 650°C. The other phases which occur, such as the carbide  $\text{M}_{23}\text{C}_6$ , the Laves phase,  $\text{Fe}_2\text{Mo}$ , the chi phase and the sigma phase dissolve little or no nitrogen, as can be learned from the literature [14].

Accordingly, the nitrogen which separates must form the chromium nitride,  $\text{Cr}_2\text{N}$ . This, again, shows only a very slight ability to dissolve other elements, such as iron and nickel [1]. The formation of  $\text{Cr}_2\text{N}$  has the result that chromium is withdrawn from the matrix, and the solubility reports for nitrogen, referred to the initial analysis of the steel, are therefore slightly too low.

As is well known, the solubility of carbon in the materials studied is very small [18-22]. In spite of the low carbon content in the steels not alloyed with nitrogen, small amounts of the cubic face-centered carbide,  $\text{M}_{23}\text{C}_6$ , could still be detected below  $900^\circ\text{C}$ . The nucleation is hindered by addition of nitrogen and the precipitation of the carbide is, therefore, shifted to longer heating times [14].

The upper temperature limits for the cubic body-centered chi phase, the tetragonal sigma phase, and the hexagonal Laves phase,  $\text{Fe}_2\text{Mo}$ , which precipitates only in the lower temperature region, are distinctly reduced by nitrogen. At the same time the incubation times are considerably extended. The cause of this effect is considered to be the austenite-forming action of the nitrogen as well as the hindering of nucleation of all phases which cannot accept this element in their lattices.

In a previous work, K. Bungardt, H. Laddach and G. Lennartz [1] showed that even the finest occupation of the grain boundaries by nitrides lead to a distinct reduction of the notch impact strength. Steels which are supersaturated with nitrogen always show a decrease of the notch impact strength after long thermal stress at temperatures above  $600^\circ\text{C}$ .

The delayed embrittlement of the nitrogen-alloyed chromium-nickel-molybdenum steels studied can be explained

as follows: The beginning of separation of the intermetallic phases is shifted to longer times because of the nitrogen addition. This causes a homogeneous austenitic structure in short-term experiments. The beginning of embrittlement is produced solely by the nitride separation at the grain boundaries. But because of the solubility-increasing action of the molybdenum, an equally great supersaturation in nitrogen is reached only at lower temperatures, in comparison to the chromium-nickel steels. At these lower temperatures the diffusion processes and the nitride formation proceed more slowly.

The different strengths of the effect of the amount of precipitate on the notch impact strength test in the nitrogen-alloyed chromium-nickel and chromium-nickel-molybdenum steels suggests differences in the separation mechanisms of the phases which form. Both the form and the position of the precipitates can have an effect. The chromium nitride forms preferentially at the grain boundaries and at the incoherent twinning boundaries. Of the intermetallic phases, the chi and sigma phases likewise form at the energetically most favorable phase boundaries. The Laves phase, in contrast, precipitates principally in the grain. With decreasing heating temperature, the rate of formation may shift in favor of the Laves phase because of the shorter diffusion distances. But because precipitates at the grain boundaries reduce the strength considerably more severely with an impact bending stress, the effect of the amount of precipitate on the notch impact strength reduction is correspondingly greater for the molybdenum-containing steels.

### Summary

Use of nitrogen as an alloying element presupposes knowledge of the solubility of nitrogen in the material and of the effect of nitrogen on the formation of phases and their effects on the

technological properties.

The tests which were done covered nitrogen-alloyed chromium-nickel and chromium-nickel-molybdenum steels with 18% Cr, 14% Ni and 2.5% Mo. The materials were supersaturated with nitrogen at temperatures in the range of 650 to 1,000°C and after solution heat treatment they were heated isothermally until thermodynamic equilibrium was established. The course of precipitation was followed as a function of the heating time and temperature. The phases were identified by X-ray measurements and the solubility limits for nitrogen determined analytically after electrochemical isolation of the precipitates. The changes in notch impact strength are also shown.

With increasing temperature, the austenitic chromium-nickel steels show increasing solubility for nitrogen. In the homogeneous phases region, the nitrogen solubility is higher in chrome-nickel-molybdenum steels than in molybdenum-free steels with the same chromium and nickel contents. The nitrogen present in the supersaturated solution separates as chromium nitride of the form  $\text{Cr}_2\text{N}$ . Chi, sigma and Laves phases form in the chromium-nickel-molybdenum steels.—Their upper temperature limits are considerably lowered by addition of nitrogen. The rate of nucleation for these intermetallic phases is also significantly reduced.

The precipitation of nitride, which occurs preferentially at the grain boundaries, distinctly reduces the notch impact strength. The other intermetallic phases formed along with chromium nitride in the chromium-nickel-molybdenum steels greatly increase the amount of precipitates. A significantly more marked embrittlement as a result of this greater total amount of precipitates was not observed.

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